

REMARKS

Claims 4, 5, 7, 10, 14, 17 and 18 are pending in the present application. Claims 1-3, 6, 8, 9, 11-13, 15, 16 and 19-21 were previously canceled. Claim 5 is currently amended.

Applicant respectfully requests reconsideration of the application in view of the foregoing amendment and the remarks appearing below, which Applicant believes places the application into condition for allowance.

Reply to USPTO's Response to Applicant's Arguments Filed on 3/24/08

On page 5 of the current Office Action, the U.S. Patent and Trademark Office (USPTO) presents a response to Applicant's arguments in his Amendment filed on March 24, 2008 ("the 3/24/08 Amendment"). In that response, the USPTO takes a position with which Applicant respectfully disagrees.

In particular, in the 3/24/08 Amendment, Applicant asserted that because the polyurethane foam of the conductiveplastics.com is conductive, it must have impurities that make it conductive. However, the USPTO subsequently replied that:

In response [to Applicant's assertion], the conductiveplastics.com website makes no mention of their foam containing impurities. The website actually remarks that their foam is known for cleanliness. There is no discussion on the website as to how clean the foam is however, since there is also no evidence of any impurities present in the foam, it is interpreted that the foam has none. This leads one of ordinary skill in the art to note that the polyurethane material alone is what makes the foam electrically conductive. Thus, since Bahten teaches a brush made from a polyurethane foam and conductiveplastics.com teaches that polyurethane foam is electrically conductive, it can be concluded that the polyurethane foam of Bahten is also electrically conductive.

Applicant respectfully points out that there are a number of factually incorrect statements and apparent misunderstandings of the contents of the conductiveplastics.com webpage in the forgoing indented quotation.

First, Applicant respectfully submits it is widely known in the field of polymers that highly pure polyurethane is nonconductive and that to make polyurethane conductive, impurities must be added and/or the urethane must be filled with a conductive material. Regarding the fact that polyurethane is nonconductive, see the attachment hereto of Polyurethane Products Corporation that states in a comparison of polyurethane to metal states that polyurethane is nonconductive. See also the "Description of the Prior Art" section of the attached U.S. Patent

No. 5,567,740 to Free, which states relative to polyurethane foam that such foam “has low electrical conductivity (or as more conveniently measured, a high electrical resistivity).” Col. 1, lines 36-37. Regarding the fact that polyurethane foam can be made conductive by adding impurities, see the Free patent, which states that a conductive foam can be made by “combining conventional polyurethane foam [which is nonconductive] and an effective amount of an anti-static agent, such as tetracyanoquinodimethane (TCNQ) or sodium perchlorate, under foam forming conditions.” Col. 1, lines 16-19. In other words, polyurethane foam is made conductive by adding impurities to the foam. Consequently, Applicant respectfully submits that the statements by the USPTO to the effect that highly pure polyurethane foam, as taught by Bahten, is conductive are incorrect.

Regarding apparent misunderstandings of the teachings of the conductiveplastics.com webpage, the conclusion that the foam of this webpage does not contain impurities does not logically flow from the fact that the webpage does not discuss impurities or how the foam is made conductive, especially since it is common knowledge in the art that polyurethane foam is nonconductive. Clearly, the makers of the conductive polyurethane foam of the conductiveplastics.com webpage either added impurities or added a conductive filler, or both, to make the base, nonconductive polyurethane conductive. Simply because the webpage does not mention this, does not mean it is not true.

Furthermore, it appears the USPTO has improperly equated the conductiveplastics.com statement that the conductiveplastics.com foam is known for its cleanliness to the issue of whether or not the foam contains impurities. This is incorrect. Applicant respectfully asserts that the term “cleanliness” as used in the context of the conductiveplastics.com foam refers to the fact that the foam does not break apart and does not slough, and therefore, does not produce particulate or other broken-off pieces that would contaminate surfaces of items that contact the foam. In this context, the term “cleanliness” has nothing whatsoever to do with describing the foam as lacking impurities.

In view of the foregoing, it is Applicant’s continued position expressed in prior arguments that it is well known in the art that highly pure polyurethane foam, such as taught by Bahten is nonconductive. Consequently, the conductiveplastics.com webpage cannot support the USPTO’s position that Bahten’s highly pure polyurethane foam is conductive.

This leaves the only possible use of the conductiveplastics.com reference as a reference to combine with the Bahten patent in an assertion that it would have been obvious to someone of ordinary skill in the art to replace Bahten's highly pure, nonconductive polyurethane foam with the conductive foam taught by the conductiveplastics.com webpage. However, this use fails because, as asserted in Applicant's 3/24/08 Amendment, such combination would destroy Bahten's explicit teachings of the need to provide highly pure foam in violation of MPEP § 2143.01(V), which states that a proposed combination of teachings can be improper where a proposed modification renders the prior art unsatisfactory for its intended purpose. Therefore, Applicant maintains below the basic positions set out in the 3/24/08 Amendment.

Furthermore, Applicant respectfully submits that if the USPTO desires to maintain its position on the electrical properties of highly pure polyurethane foam, it must provide actual conclusive evidence of such pursuant to MPEP § 2144.03. In this connection, Applicant respectfully asserts that the conductiveplastics.com webpage does not constitute such conclusive evidence because it simply does not address how the foam is made conductive. Therefore, there is no reasonable way to logically conclude that the conductiveplastics.com is, in fact, highly pure, for at least the reasons discussed above.

Rejections Under 35 U.S.C. § 103(a)

Bahten/Hawn/Lur et al./ConductivePlastics.com

Claims 7, 10, 14, 17 and 18 stand rejected under 35 U.S.C § 103(a) as being obvious in view of a combination of U.S. Patent No. 6,182,323 to Bahten, the Hawn IBM Technical Disclosure Bulletin, U.S. Patent No. 6,743,721 to Lur et al., and conductiveplastics.com Webpage. The USPTO asserts that Bahten teaches all of the limitations of these claims, except for the feature of electrically grounding the rotating microelectronics wafer cleaning member. Applicant respectfully disagrees.

Bahten discloses porous polymeric scrubbing brushes for cleaning particulate contaminants from, among other things, microelectronics wafers. Bahten also discloses that these brushes are used in wafer cleaning apparatuses. The Bahten brushes are made of polymers, such as polyvinyl acetal and polyurethane, containing very little impurities.

The Hawn Bulletin describes removing unwanted electrostatic charges from photoconductive plates using a soft grounded brush with multiple conductive points that come into intimate contact with the surface being discharged.

Lur et al. disclose a microelectronics wafer having a dielectric surface. Lur et al. also disclose a cluster tool having various wafer processing stations for fabricating and handling wafers.

The conductiveplastics.com Webpage discloses a conductive polyurethane foam that is touted for its cleanliness, i.e., lack of sloughing and particulation.

Turning now to the rejected claims, independent claim 10 as previously presented includes the limitation of "cleaning said surface of said microelectronics wafer with a conductive rotating wafer-cleaning member so as to remove at least some of the surface contaminants, and so as to simultaneously create an electrical ground path between said surface and an electrical ground through said conductive rotating wafer-cleaning member." [Emphasis added.] Similarly, independent claim 17 as previously presented includes the limitation of "a conductive rotating wafer-cleaning member operatively configured to engage said surface of microelectronics wafer in said wafer cleaning region so as to remove contaminants from said surface and provide part of a grounding path between said microelectronics wafer and said electrical ground for removing electrical charge from said microelectronics wafer." [Emphasis added.]

Assuming for the sake of argument that the Conductive Plastics webpage is proper prior art (it is not clear what the 2003 copyright notice at the bottom of the webpage applies to), Applicant respectfully submits that the present rejection is improper because the assertion that the Conductive Plastics conductive foam could be used in place of the high-purity foam of the Bahten wafer-cleaning brushes renders Bahten's brushes unsatisfactory for their intended purpose in violation of MPEP § 2143.01(V).

MPEP § 2143.01(V) states that a proposed combination of teachings can be improper where a proposed modification renders the prior art unsatisfactory for its intended purpose. As set forth in the response to a prior Office Action in this application, Bahten discloses polymer foam microelectronics-wafer-cleaning brushes having very low levels of impurities as compared to conventional (non-conductive) polymer foam brushes. See, e.g., Bahten's Table 1A, col. 4. Indeed, Bahten touts that the "present devices have fewer impurities and/or particulates than conventional foam products." Bahten patent, col. 4, lines 28-29. Bahten further asserts that "Based on Table 1A, it is clear that the present invention provides a much cleaner device than conventional ones." Bahten patent, col. 4, lines 43-44. Consequently, Bahten teaches very

clean, non-conductive brushes for providing exceptional micro-electronics wafer cleaning capability.

The Conductive Plastics webpage describes conductive flexible polyurethane foam and pink antistatic foam for packaging. The webpage states: "An outstanding advantage for using Conductive Plastics conductive foam is cleanliness. There is no sloughing. It's non-corrosive and does not particulate." From the photograph and description of the application of the Conductive Plastics' foam (i.e., packing material), it is clear that the Conductive Plastics' foam is very low density foam and has a character much different from the foam of Bahten, as those skilled in the art would readily appreciate.

Applicant respectfully asserts that the packing foam of the Conductive Plastics is of such a different character than the foam of the Bahten brushes that it is improper for the USPTO to assert the combination without further evidence that the references could indeed be combined to produce the same cleaning prowess of the Bahten brushes. In particular, while the Conductive Plastics webpage addresses the packing foam's "cleanliness," those skilled in the art would readily understand that cleanliness in the realm of packing materials (where cleanliness is measured in terms of lack of macro- or meso-scale sloughing and particulation) is far different from cleanliness in the field of microelectronics wafer cleaning wherein cleanliness is measured in terms of microparticles.

Furthermore, while Conductive Plastics notes the cleanliness of its packing foam, this does not address the purity of the foam in terms of impurities that make it conductive. Surely the Conductive Plastics packing foam contains impurities that make it conductive. While these impurities may not impact the macro- or even meso-scale cleanliness of the foam, Applicant respectfully asserts that they may indeed impact the micro-scale cleanliness needed in the micro-scale regime of microelectronics wafer cleaning (as those skilled in the art would readily recognize).

In view of the foregoing, Applicant respectfully asserts that because the Conductive Plastics' packing foam likely includes impurities that make it conductive and also less clean than the Bahten brushes in terms set forth in the Bahten patent, the combination is improper as being contrary to Bahten's teachings of a very low impurity foam for enhanced cleaning capabilities. In addition, Applicant respectfully asserts that the combination is improper because it does not address the fact that there is no evidence that the Conductive Plastic's packing foam is truly

clean in the micro-scale regime needed for microelectronics wafer cleaning. In view of the foregoing, if the USPTO continues the present rejection, Applicant respectfully requests evidence that the Conductive Plastics packing foam could in fact provide the superior wafer cleaning ability of Bahten's low-impurity non-conductive brushes. Otherwise, Applicant believes the combination is improper because the substitution of the Conductive Plastics' foam for Bahten's foam would render the Bahten brushes unsatisfactory for their intended purpose of providing superior wafer-cleaning capability to conventional higher-impurity wafer-cleaning brushes.

Because the base combination of the Conductive Plastics' teachings with Bahten's teachings is improper for at least the foregoing reasons, Applicant respectfully requests that the Examiner withdraw the present rejection.

Bahten/Hawn/Lur et al./Kitamura et al./ConductivePlastics.com

Claims 4 and 5 stand rejected under 35 U.S.C § 103(a) as being obvious in view of a combination of the Bahten, Hawn Bulletin, Lur et al., and Kitamura et al. references, each discussed above. Applicant respectfully disagrees.

The Bahten, Hawn Bulletin, Lur et al., and Conductive Plastics references are as described above relative to the obviousness-type rejection.

Kitamura et al. disclose a charge removal brush that includes a number of long, conductive filamentous elements for removing charges from an object when the charge removal brush comes in contact with the object, is disclosed. The charge removal brush includes a metal shaft rotatable about the axis thereof, a strip-like woven cloth including a base cloth and long conductive filamentous elements uniformly planted in the substantially entire surface of the base cloth, the strip-like woven cloth being spirally wound on the metal shaft with no gap, and a conductive fiber is woven into the base cloth in a state that the conductive fiber runs along the center line of the base cloth, which is extended in the lengthwise direction of the base cloth.

As discussed above relative to the obviousness-type rejection in view of the Bahten/Hawn/Lur et al./conductiveplastics.com combination, Applicant believes that at least the combination of the Conductive Plastics' teachings with the Bahten teachings is improper relative to the claims from which claims 4 and 5 depend. The additional combination with the Kitamura et al. patent, in Applicant's view, does not remedy the shortcomings of this improper

combination. Consequently, it is Applicant's position that the Bahten/Hawn/Lur et al./conductiveplastics.com/Kitamura et al. combination does not render claims 4 and 5 obvious.

For at least this reason, Applicant respectfully requests that the Examiner withdraw the present rejection.

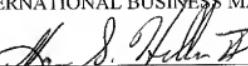
CONCLUSION

In view of the foregoing, Applicant submits that claims 4, 5, 7, 10, 14, 17 and 18 are in condition for allowance. Therefore, prompt issuance of a Notice of Allowance is respectfully solicited. If any issues remain, the Examiner is encouraged to call the undersigned attorney at the number listed below.

Respectfully submitted,

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Attachments:

Portion of webpage of Polyurethane Products Corporation from
www.polyprod.com/ucomp.html
U.S. Patent No. 5,567,740 to Free

2749998.1



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Comparisons

Polyurethanes have definite advantages over plastics, conventional rubber and metals, which make them a **better substitute in applications** where these materials are normally used.

... vs. Rubber

- high abrasion resistance
- high cut, tear resistance
- superior load bearing
- thick section molding
- colorability
- oil resistance
- ozone resistance
- radiation resistance
- broader hardness range
- castable nature
- low pressure tooling

... vs. Metal

- lightweight
- noise reduction
- abrasion resistance
- less expensive fabrication
- corrosion resistance
- resilience
- impact resistance
- flexibility
- easily moldable
- non-conductive
- non-sparking

... vs. Plastic

- high impact resistance
- elastic memory
- abrasion resistance
- noise reduction
- variable coefficient of friction
- resilience
- thick section molding
- lower cost tooling
- low temperature resistance
- cold flow resistance
- radiation resistance

Some specific properties of Polyurethanes when examined show it to be a more practical choice as compared to those of rubber, metal and plastic.

• Abrasion Resistance:

The outstanding abrasion resistance of Cast polyurethanes has resulted in thousands of successful applications. In laboratory tests as well as in field applications, Cast Polyurethanes show a definite wear advantage over many other materials. The following figure illustrates a comparison of abrasion properties of Polyurethane with rubbers and plastics.



US005567740A

United States Patent [19]
Free

[11] **Patent Number:** **5,567,740**
[45] **Date of Patent:** **Oct. 22, 1996**

[54] **CONDUCTIVE POLYURETHANE FOAM COMPOSITIONS AND METHOD FOR PRODUCING SAME**

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[73] Assignee: **Foamex, L.P.**, Linwood, Pa.

[21] Appl. No.: **483,377**

[22] Filed: **Jun. 7, 1995**

[51] Int. Cl.⁶ C08G 08/38; A01B 1/00

[52] U.S. Cl. 521/128; 252/500; 521/123

[58] Field of Search 521/123, 128;
252/500

[56] **References Cited**

U.S. PATENT DOCUMENTS

5,180,755 1/1993 Yasunaga et al. 521/116

*Primary Examiner—Morton Foelak
Attorney, Agent, or Firm—Connolly & Hutz*

[57] **ABSTRACT**

The present invention relates to three-dimensional expanded polyurethane foam materials, such as flexible reticulated polyurethane foam compositions, that are electrically conductive and have antistatic properties. More specifically, the invention relates to a polyurethane foam having long-lasting and reliable electrical conductivity characteristics and a volume resistivity of approximately 10^{13} ohm-cm or less at ambient room temperature (about 70° F.). This foam is produced by combining conventional polyurethane foam-forming reactants and an effective amount of an antistatic agent such as tetracyanoquinodimethane (TCNQ) or sodium perchlorate under foam-forming conditions. In one preferred embodiment, the conductive foam is subsequently reticulated by momentary exposure to a flame front.

12 Claims, No Drawings

**CONDUCTIVE POLYURETHANE FOAM
COMPOSITIONS AND METHOD FOR
PRODUCING SAME**

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to three-dimensional expanded polyurethane foam materials, such as flexible reticulated polyurethane foam compositions, that are electrically conductive and have antistatic properties. More specifically, the invention relates to a polyurethane foam having long-lasting and reliable electrical conductivity characteristics and a volume resistivity of approximately 10^{12} ohm-cm or less at room temperature (about 70° F.). This foam is produced by combining conventional polyurethane foam-forming reactants and an effective amount of an antistatic agent, such as tetracyanoquinodimethane (TCNQ) or sodium perchlorate, under foam-forming conditions. In one preferred embodiment, the conductive foam is subsequently reticulated by momentary exposure to a flame front.

2. Description of the Prior Art

It has long been known that it is not possible to generate an explosion of any fuel/air mixture in the presence of reticulated polyurethane foam structures. Because of this characteristic of reticulated polyurethane foam and the additional benefits of light weight, minimal reduction in a fuel tank's usable space and attenuation of violent surging of fuel, reticulated polyurethane foam structures have found extensive use in military aircraft and land vehicles. These properties reduce the vulnerability of these vehicles by providing protection against explosive ballistic hits, explosions following fuel tank rupture, explosive static discharge and explosions caused by lightning.

Unfortunately, the use of foam can give rise to a different danger. Since the foam has a low electrical conductivity (or as more conveniently measured, a high electrical resistivity), there can be a buildup of electrostatic charges and the electrostatic charges can result in sparking, leading to a fire or explosion within the non-foam containing areas of the fuel tank. The build-up of electrostatic charges can also adversely effect sensitive aircraft instrumentation.

Consequently, it is an object of this invention to provide a foam for fuel tanks which minimizes the possibility of fuel explosion from gunfire, electric ignition and lightning. It is a further object of this invention to provide a foam which has a higher electrical conductivity needed to minimize the danger of sparking caused by the build-up of electrostatic charges. It is a further object of this invention to provide fuel tanks which minimize the release of fuel in the event of rupture and which resist sparking due to the build-up of electrostatic charge.

U.S. Pat. No. 4,886,626 (Copp et al.) describes a conductive polyurethane foam which contains a charge transfer agent selected from the group consisting of tetracyanoethylene (TCNE), picric acid and analogs thereof. These foams exhibit electrical resistivities (i.e., volume resistivities) of 10^{12} ohm-cm or less. However, these foams suffer from the disadvantage that the charge transfer materials used in the foam are dangerous to handle. For example, TCNE is highly toxic and picric acid and its derivatives are explosive.

SUMMARY OF THE INVENTION

It is an object of the invention to provide an electrically conductive polyurethane foam that is suitable for use as a filler material in fuel containers or tanks, particularly in

vehicles having combustion powered engines, wherein the polyurethane foam does not contain any highly toxic substances such as TCNE.

It is another object of the invention to provide a stable, reliable and long-lasting electrically conductive reticulated polyurethane foam structure that retains its conductivity characteristics despite repeated mechanical abrasion and use at low temperatures (e.g., 0° F. to -30° F.), high temperatures (e.g., 120° F. to 160° F.), organic fluids and aqueous fluids.

A further object of the present invention is to provide an electrically conductive reticulated polyurethane foam having a void volume greater than at least about 80%, and preferably more than about 90%, using relatively small quantities of the agent conferring electrical conductivity in the foam forming reaction mixture.

Another object of the present invention is an electrically conductive thermally reticulated polyurethane foam prepared from a polyol and an isocyanate and containing about 0.08 to 0.20 parts of TCNQ per hundred parts by weight of polyol (php) in the foam forming mixture. In a preferred embodiment of the present invention, the electrically conductive thermally reticulated polyurethane foam contains from 0.08-0.15 php of TCNQ in the foam forming mixture.

20 A further object of the present invention is an electrically conductive thermally reticulated polyurethane foam prepared from a polyol and an isocyanate and containing about 0.08 to 0.20 parts of TCNQ per hundred parts by weight of polyol (php) in the foam forming mixture. In a preferred embodiment of the present invention, the electrically conductive thermally reticulated polyurethane foam contains from 0.08-0.15 php of TCNQ in the foam forming mixture.

25 A still further object of the present invention is an electrically conductive thermally reticulated polyurethane foam prepared from a polyol and an isocyanate and containing about 0.06 to 1.00 parts of sodium perchlorate (NaClO_4) per hundred parts by weight of polyol (php), preferably 0.06 to 0.80 php sodium perchlorate and most preferably 0.075 to 0.80 php sodium perchlorate, in the foam forming mixture. Since sodium perchlorate, by itself, is a potentially explosive material, it is preferable to use a solution of sodium perchlorate in an aqueous or organic solvent during the foam forming procedure. A preferred sodium perchlorate solution is MP100 (from Akishima Chemical Industries Co., Ltd., Tokyo, Japan), which is a solution of 30-40% by weight sodium perchlorate in diethylene glycol methyl ether. Accordingly, when MP100 is used as the source of sodium perchlorate in the foam forming mixture, the following amounts of MP100 are used: 0.20 to 2.50 parts of MP100 per hundred parts by weight of polyol (php), preferably 0.20 to 2.00 php MP100 and most preferably 0.25 to 2.00 php MP100, in the foam forming mixture.

30 It is another object of the present invention to provide a polyurethane foam composition having a non-electrical volume resistivity of less than about 10^{12} ohm-cm (at room temperature) and a lower volume resistivity at low temperatures (e.g., 0° F. to -30° F.) than conventional polyurethane foams.

35 The objects of the invention are achieved by providing an electrically conductive polyurethane foam, wherein the electrical resistivity of the foam is desirably decreased to approximately 10^{12} ohm-cm or less by the integral incorporation of relatively small yet effective amounts of a specific antistatic agent (i.e., TCNQ or sodium perchlorate) into the structure of the foam during foam formation.

40 Advantageous polyurethane foam forming reactants include well known polyester and polyether polyols and diisocyanate compounds. Additional reaction materials include water, catalyst compounds, and cell control agents. According to the invention, the effective amount of antistatic

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agent (e.g., TCNQ or sodium perchlorate) ranges from about 0.08 to 0.20 parts per hundred parts polyol (php), preferably 0.08 to 0.15 php and most preferably 0.10-0.15 php, when the antistatic agent is TCNQ and from about 0.06 to 1.00 php, preferably 0.06 to 0.80 php and most preferably 0.075 to 0.80 php, when the antistatic agent is sodium perchlorate.

Surprisingly, the electrical conductivity properties afforded by in situ incorporation of TCNQ or sodium perchlorate survive the exotherm (on the order of about 300° F.) accompanying polyurethane foam formation, subsequent reticulation of the foam under plasma temperature conditions (of about 2000° F. or more), monolithic abrasion, use at low temperatures (e.g., 0° F. to -30° F.) and high temperatures (e.g., 120° F. to 160° F.) and long-term exposure to aqueous and organic fluids. Accordingly, the foam products of the invention are particularly well suited for use as an antistatic material, for example as a filler in aircraft fuel tanks or as a packaging material for delicate electronic components.

According to the invention, a conductive polyurethane foam is formed in situ, by known means, using conventional foam forming reactants comprising one or more polyols, an isocyanate compound or composition, and an effective amount of an antistatic agent such as TCNQ or sodium perchlorate, for providing said polyurethane foam with an electrical resistivity of less than 1×10^{12} ohm-cm at ambient room temperature (about 70° F.).

According to the present invention a polyether or polyester urethane foam is formed from: isocyanate and hydroxyl containing (polyol) reactants by known means, but with the antistatic agent incorporated into the reaction mixture prior to foam formation. The resulting polyurethane foam has a solids volume of from about 2% to about 3.3% and a void volume of from about 96.7% to about 98%. The resulting polyurethane foam may thereafter be reticulated. For example, the foam can be reticulated according to the thermal reticulation method taught in Geen et al., U.S. Pat. No. 3,175,025 which is incorporated herein by reference or by any of the other thermal reticulation methods known in the art. In preparing electrically conductive polyurethane foams for use as fuel tank filler materials, graft polyols are preferred as the polyol constituent of the foam. One preferred graft copolymer is an ethylene oxide propylene oxide ether of glycerin to which a copolymer of styrene and acrylonitrile has been grafted. The invention is not limited, however, to the use of these graft materials as the polyol constituent. The flexible three dimensional polyurethane foams of the invention may be prepared by reacting isocyanate compounds with polyether polyols, polyester polyols, mixtures of polyether polyols and copolymer polyols such as, for example, the grafted polyether containing styrene and acrylonitrile as described above, in the presence of the antistatic agent. The resulting electrically conductive polyurethane foams exhibit a resistivity of about 10^{12} ohm-cm or less at ambient room temperature, and retain this advantageously decreased electrical resistivity despite exposure to exothermic foam forming conditions, relatively violent high temperature reticulation procedures, immersion in water or fuel, use at low temperatures (e.g., 0° F. to -30° F.) and high temperatures (e.g., 120° F. to 160° F.) and dry heat aging.

DETAILED DESCRIPTION OF THE INVENTION

The invention is described with reference to a number of examples and embodiments, and with reference to a number of comparative tests. It will be understood by skilled prac-

titioners that these examples, embodiments and comparisons are illustrative only and do not limit the scope of the invention.

The polyurethane foams of the present invention may be prepared using the one shot or the pre-polymer methods that are well known to the art and in which hydroxyl containing ingredients (polyols) and polyisocyanates are combined in the presence of well known catalysts, blowing agents, foam stabilizers, flame retardants, pigments and extenders. Polyester based polyurethanes, polyether based polyurethanes, copolymer polyol based polyurethanes and mixtures of these substances may be used in making the conductive foams of the present invention, although polyether foams are preferred.

The polyisocyanate ingredients that are useful in the present invention include, but are not limited to, toluene diisocyanate (TDI), which is preferred, and polymers of diphenylmethane 4,4'-diisocyanate (MDI).

Representative hydroxyl containing ingredients for use in the invention include polyester and polyether polyols such as, for example, the polypropylene glycol adipate glycerine ester and the ethylene oxide propylene oxide ether of glycerin. Graft copolymers of hydroxyl containing constituents which may also be employed as polyol constituents in practicing the invention include ethylene oxide propylene oxide ether of glycerin to which various amounts (between 13 and 45%) of a copolymer of styrene and acrylonitrile have been grafted. The preferred graft polyol for use in the present invention is a polymer consisting of the ethylene oxide propylene oxide ether of glycerin to which 45% of a copolymer of styrene and acrylonitrile has been grafted.

According to the invention, polyether or polyester polyols are reacted in situ under the usual polyurethane foam forming conditions with an isocyanate and small amounts of an antistatic agent (e.g., from about 0.08 to 0.20 php of TCNQ or from about 0.06 to 1.00 php of sodium perchlorate). The foam forming reaction is conducted in the presence of the usual foam forming ingredients including catalyst compounds (such as tertiary amines and organo tin compounds) cell control agents and water to provide a polyurethane foam having an electrical resistivity of about 10^{12} ohm-cm or less at ambient room temperature. The electrically conductive polyurethane foam product may be advantageously reticulated with the thermal reticulation technique taught in Geen, U.S. Pat. No. 3,750,025. In this procedure the three dimensional foam product is placed in a sealed gas-filled chamber filled with a combustible gas and the gas ignited to produce an explosion and a flame front in which the foam is exposed to momentary plasma temperatures in excess of 2000° C. However, any of the thermal reticulation procedures known in the art can be used to reticulate the foam of the present invention.

It has been found that polyurethane foams made with in situ antistatic agents are stable and retain their enhanced electrical conductivity properties at high temperatures (e.g., 120° F. to 160° F.), low temperatures (e.g., 0° F. to -30° F.) and long term immersion in aqueous and organic liquids.

The invention will be illustrated in the following tables and working examples. With reference to the examples, foam formulations are based on 100 parts by weight of polyol, as is customary. All other components are added in parts by weight per hundred parts by weight of polyol (php), unless otherwise noted. "E n" is a convenient shorthand notation for the expression " $\times 10^n$ ".

The volume resistivity of the polyurethane foam product was measured using the following equipment and proce-

dures (described in ASTM-D-257-78 and MIL-F-87260 [USA]). A 10" diameter and 1" thick sample of foam was placed on a base electrode. An inner electrode with a 10.6 cm diameter and an outer guard ring with a 15.2 cm inner diameter were placed on top of the foam sample. The electrodes were centered directly over each other to produce a vertical "field" between the plates. The megohmmeter (Beckman Megohmmeter model L-8 or equivalent) voltage was set to 500 volts and the variable resistance adjusted until a resistance reading was obtained on the meter. After a one minute stabilization period, the resistance was recorded. Volume resistivity was calculated as follows:

$$\text{ev} = \frac{\text{measured resistance (ohms)} \times 144.07 \text{ (cm}^2\text{)}}{\text{sample thickness (inches)} \times 2.54 \text{ (cm/inch.)}}$$

This procedure and apparatus were used for the measurements reported in the Examples.

It has been found that foaming with *in situ* TCNQ or sodium perchlorate produces adequate antistatic properties in conventional polyurethane foams with as little as about 0.08 phr of TCNQ or about 0.06 phr of sodium perchlorate.

Although thermal reticulation of the foam products is preferred (due to cost and speed considerations), the other reticulation techniques that are well known in the art including, for example, immersion of the foam in dilute alkaline solution (this works for ester foams only) and exposure to high pressure water and ultra sound may also be used to reticulate conductive foams made with the antistatic agents according to the invention.

The electrically conductive foam materials of the present invention may be employed in a variety of military, industrial, and consumer applications. When shaped in the appropriate configuration and sized to the proper dimension, these foam products can be used, for example, as packaging material for voltage sensitive computer parts to protect them against static electric discharge (e.g., Large Scale Integrated Circuits), in medical applications (e.g., as grounding mats for operating room equipment) or as an antistatic carpet underlay. A particularly preferred application for these foams is as a filler material in vehicular fuel tanks and especially those installed in military aircraft or racing cars.

The following examples will aid in explaining, but should not be deemed as limiting, the practice of the present invention. In all cases, unless otherwise noted, all parts and percentages are by weight.

It is understood that the foregoing description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

EXAMPLE 1

A polyol mixture is prepared from 50 parts of a polyether polyol (Veranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 58.2 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 4.8 parts water, 0.5 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.2 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI), 0.08 parts TCNQ and 5.0 parts NMP (N-methyl pyrrolidone). The isocyanate index was 110 (i.e., a 10% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanate were combined in a vessel and mixed thoroughly to form a mixture. The TCNQ was added as a solution of the TCNQ in the NMP. The isocyanate was then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.4 lbs/cu ft.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table 1.

EXAMPLE 2

A polyol mixture is prepared from 50 parts of a polyether polyol (Veranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 38.4 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 25.5 parts of TDI (TD65 from Olin Corp.), 5.6 parts water, 0.5 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.0 part of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 0.1 parts TCNQ. The isocyanate index was 105 (i.e., a 5% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanates were combined in a vessel and mixed thoroughly to form a mixture. The TCNQ was added in powder form (TCNQ powder was obtained from TCI America, 9211 N. Harbor Gate Street, Portland, Ore. 97203). The isocyanates were then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.2 lbs/cu ft.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table 1.

EXAMPLE 3

A polyol mixture is prepared from 50 parts of a polyether polyol (Veranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 38.4 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 25.5 parts of TDI (TD65 from Olin Corp.), 5.6 parts water, 0.5 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.0 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 0.2 parts TCNQ. The isocyanate index was 105 (i.e., a 5% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanates were combined in a vessel and mixed thoroughly to form a mixture. The TCNQ was added in powder form (TCNQ powder obtained from TCI America, Portland, Oreg.). The isocyanates were then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.2 lbs/ft³.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table I.

EXAMPLE 4

A polyol mixture is prepared from 50 parts of a polyether polyol (Voranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 48.9 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 4.1 parts water, 0.25 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.2 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 0.25 parts MP100 (from Akishima Chemical Industries Co., Ltd., Tokyo, Japan). The isocyanate index was 110 (i.e., a 10% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanate were combined in a vessel and mixed thoroughly to form a mixture. The isocyanate was then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.6 lbs/ft³.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table I.

EXAMPLE 5

A polyol mixture is prepared from 50 parts of a polyether polyol (Voranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 48.9 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 4.1 parts water, 0.25 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.2 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 0.50 parts MP100 (from Akishima Chemical Industries Co., Ltd., Tokyo, Japan). The isocyanate index was 110 (i.e., a 10% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanate were combined in a vessel and mixed thoroughly to form a mixture. The isocyanate was then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.6 lbs/ft³.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table I.

EXAMPLE 6

A polyol mixture is prepared from 50 parts of a polyether polyol (Voranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 48.9 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 4.1 parts water, 0.25 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.2 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 1.0 parts MP100 (from Akishima Chemical Industries Co., Ltd., Tokyo, Japan). The isocyanate index was 110 (i.e., a 10% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanate were combined in a vessel and mixed thoroughly to form a mixture. The isocyanate was then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.6 lbs/ft³.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table I.

EXAMPLE 7

A polyol mixture is prepared from 50 parts of a polyether polyol (Voranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Arco). The polyol mixture (100 total parts) is reacted with 48.9 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 4.1 parts water, 0.25 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Niax A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.2 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 2.0 parts MP100 (from Akishima Chemical Industries Co., Ltd., Tokyo, Japan). The isocyanate index was 110 (i.e., a 10% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanate were combined in a vessel and mixed thoroughly to form a mixture. The isocyanate was then added to the mixture and

further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.6 lbs/ft³.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at various temperatures. The results are reported in Table 1.

EXAMPLE 8 (COMPARISON)

A polyol mixture is prepared from 50 parts of a polyether polyol (Voranol 3010—Dow Chemical) and 50 parts of a graft polyol (HS100 from Aroco). The polyol mixture (100 total parts) is reacted with 58.2 parts of TDI (toluene diisocyanate—TD80 from Olin Corp.), 4.8 parts water, 0.5 parts tin catalyst (T-9 from Air Products), 1.0 part amine catalyst 1 (C124—Nixa A-1, a proprietary tertiary amine product of Air Products, in dipropylene glycol in a ratio of 1:6), 1.1 parts amine catalyst 2 (NEM from Air Products), 1.2 parts of a silicone surfactant (L6202 from OSI), 2.0 parts of a pigment (4824 from Ferro/PDI) and 5.0 parts NMP (N-methyl pyrrolidone). The isocyanate index was 110 (i.e., a 10% excess of isocyanate over the stoichiometric amount).

All of the above ingredients except the isocyanate were combined in a vessel and mixed thoroughly to form a mixture. The isocyanate was then added to the mixture and further mixing was performed to form a final mixture. The final mixture was then poured into a box shaped vessel and allowed to rise into a foam. After the foam had stopped rising, the vessel containing the foam was placed into an oven at 250° F. for one hour to cure. After the one hour curing period, the foam was removed from the vessel as the final foam product.

The foam produced in this example had a density of 1.5 lbs/ft³.

The resistivity (volume resistivity in ohms-cm) of the foam produced in this example was measured at room temperature. The result is reported in Table 1.

TABLE 2

	Polarity of 5000 Volt Charge	+	-
5	Dissipation Time for Foam of: Example 1	0.71 seconds	0.72 seconds
	Dissipation Time for Foams of: Example 8	>500 seconds	320 seconds

From the above examples it can be seen that the foams of the present invention that contain TCNQ or sodium perchlorate have a reduced electrical resistivity and an excellent static decay rate in comparison to conventional polyurethane foams with identical or equivalent compositions which do not contain TCNQ or sodium perchlorate.

What is claimed is:

1. A three dimensional electrically conductive plastic foam structure comprising a polyurethane foam containing an effective amount for lowering the volume resistivity of said foam of an antistatic agent consisting essentially of tetracyanoquinodimethane.

2. A three dimensional electrically conductive structure according to claim 1, wherein said structure is prepared by reacting a polyol and an isocyanate and comprises 0.08 to 0.20 parts per hundred parts by weight of said polyol of said tetracyanoquinodimethane as said antistatic agent.

3. A three dimensional electrically conductive structure according to claim 1, wherein said polyurethane foam comprises a reticulated polyurethane foam.

4. A three dimensional electrically conductive structure according to claim 1, wherein said polyurethane foam is formed from at least one polyol and at least one isocyanate and further wherein said antistatic agent is tetracyanoquinodimethane which is dissolved in a suitable solvent.

5. A three dimensional electrically conductive structure according to claim 1, wherein said polyurethane foam is formed from a reaction mixture containing at least one polyol and at least one isocyanate and further wherein said antistatic agent is tetracyanoquinodimethane which is not dissolved in a solvent but is added directly to the reaction mixture.

6. A three dimensional electrically conductive structure according to claim 2, wherein said polyurethane foam contains 0.08 to 0.15 parts per hundred parts by weight of said polyol of said tetracyanoquinodimethane.

7. A three dimensional electrically conductive structure according to claim 2, wherein said polyurethane foam contains 0.10 to 0.15 parts per hundred parts by weight of said polyol of said tetracyanoquinodimethane.

8. A three dimensional electrically conductive structure having a volume resistivity at about 70° F. of less than 10¹³ ohm-cm, comprising a polyurethane foam containing an effective amount for reducing the electrical resistivity of said foam to less than 10¹² ohm-cm of an antistatic agent consisting essentially of tetracyanoquinodimethane incorporated into said foam in situ.

9. A three dimensional electrically conductive structure

The static decay properties of the foams of Examples 1 and 8 were compared by applying a 5000 volt charge to a 3" by 5" by 50" piece of the foam at about 70° F. (room temperature) and measuring the time required for the foam to dissipate 90% of the charge. Each piece was subjected to a positive 5000 volt charge and a negative 5000 volt charge. The results are shown in Table 2.

TABLE 1

Temp.	Volume Resistivity							
	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8
70° F.	5.3E11	8.3E11	3.4E12	1.1E12	4.1E11	3.3E11	1.5E11	1.19E14
20° F.	5.7E13	1.3E13	2.7E14	5.9E13	5.1E13	3.1E13		
0° F.	6.8E13	5.7E14	1.0E14		3.4E14	2.8E14	1.6E14	
-30° F.		8.5E14	1.4E15		>1.0E14	8.5E14		

according to claim 8, wherein said antistatic agent is tetracyanoquinodimethane which is present in an amount of from about 0.08 to 0.20 php.

10. A method of preparing an electrically conductive polyurethane foam composition which comprises reacting, under foam forming conditions, at least one polyester or polyether polyol with an isocyanate compound in the presence of an effective amount for lowering the electrical resistance of said polyurethane foam of an antistatic agent consisting essentially of tetracyanoquinodimethane.

11. A method according to claim 10, wherein said electrically conductive polyurethane foam has an electrical resistivity of less than 10^{12} ohm-cm at about 70° F.

12. A method according to claim 10, wherein said antistatic agent is tetracyanoquinodimethane and the amount of said tetracyanoquinodimethane in said polyurethane foam composition is from about 0.08 to 0.20 php.

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